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The Action of Amines on the Chlorides of Orthosulphobenzoic Acid.

A Dissertation
Presented to the Board of University Studies
of the Johns Hopkins University for the
Degree of Doctor of Philosophy

By

Elmer P. Kohler.

1892.

I gladly avail myself of this opportunity to express my sincere thanks for the assistance that I gladly received during the earlier part of my course of training in my studies.

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The action of phosphorus pentachloride upon [illegible] and sodium [illegible] in anhydrous ether they obtained white rhombic needles which melted at 73° and had the composition $C_6H_4SO_3Cl_2$. A study of the reactions of the substance and its analogues — phthalyl chloride — it is a symmetrical di-chloride, having the structure [illegible]. Based mainly on its ability to form chloro-esters. They found that the chlor-

$$C_6H_4 \begin{cases} COCl \\ SO_2Cl \end{cases} + HOC_2H_5 = C_6H_4 \begin{cases} CO.OC_2H_5 \\ SO_2Cl \end{cases}.$$

When the chloro-ether formed or the original chloride was boiled with absolute alcohol an acid ether having the constitution $C_6H_4 < {CO.OC_2H_5 \atop SO_2OH}$ was obtained. These reactions

differently with alcohol and the most

Noteworthy exhibition is that one is united

with carbon

All the decompositions of the chloride which they studied were in harmony with this

view.

Later Coates[1], while studying the action of

some substances, obtained some quite unexpected results. He found

and the chloride was boiled

for

solution $C_{19}H_{16}O_3N_2S$, corresponding to a di-

(1) Inaug. Diss. Johns Hopkins University 1891.

amilide of orthosulphobenzoic
and the general properties of an
ilide. Further he found that when dry ani-
line and the dry chloride are allowed
to react directly, two compounds are formed.
One of these has the composition $C_{13}H_9SNO_3$
corresponding to orthosulphobenzanil $C_6H_4\langle CO \atop SO_2\rangle NC_6H_5$.
[illegible]
compound obtained in the presence of water
differing
from it in all its physical
properties, decomposes below its melting point
[illegible]
an entirely different crystal form.
[illegible]
having the composition of a dianilide of
orthosulphobenzoic acid were therefore
obtained on the product of the action of
aniline upon orthosulphobenzoyl chloride.
The three isomerides gave similar re-

work of Dr. Coates could obtain no experimental evidence as at the suggestion of Prof. Clemson I undertook the investigation of which the results thus far obtained are

Benzoate by the method of Clemson and Burton. It was found extremely difficult to obtain from some of the more soluble constituents

sulphuric nitric acid was evaporated to
dryness on the water-bath, the residue
to a fine powder, placed upon a filter and
washed with small quantities of absolute
alcohol until the washings, on evaporation,
left nothing except a small quantity of
pure acid-ammonium phosphate soluble.
One or two precipitations from water of
the salt thus washed were usually sufficient
to give an absolutely pure substance.
The pure acid-ammonium salt thus obtained
salt in order to avoid subsequent con-
tamination of the chloride by chlor-phos-
phuret of nitrogen which, as known by
Wöhler, is one of the products of phosphoric
acid chloride upon ammonium salts. This
transformation is readily accomplished
by first converting the acid ammonium

were distilled off in a water-bath as far as possible, and the residue poured into a large quantity of cold water. On boiling down this, it was washed with [illegible] last washings nor a solution obtained by decomposing a small quantity of the chlorides with boiling water gave a reaction [illegible] dilute sulphuric acid and solid caustic potash. Thus prepared, the product is a colorless oil which assumes a waxy consistency on standing over sulphuric acid [illegible].

Behavior of the Chlorides

The [illegible] product [illegible] completely in anhydrous ether. All efforts to get it in a crystalline condition [illegible]

perfectly colorless solution is allowed to evaporate rapidly, the oil separates and unchanged. If, on the other hand, it is evaporated slowly in a sulphuric acid desiccator, the solution gradually becomes yellow and cloudy, as the oil begins an experiment frequently odor persists. This seems to point to a gradual decomposition of the chlorides in the ethereal solution. An attempt was made to increase the amount of the decomposition in order, if possible, to determine its nature. For this purpose the ethereal solution was boiled in a flask connected with a reflux condenser, but no decomposition took place under these conditions, the solution remaining clear and colorless. That the decomposition is not

yellow oil mentioned above is washed with hot water until the color disappears, dried and dissolved in ether it becomes colored as before and it seems that these bases can be repeated indefinitely with the same results.

Chloroform. -

The Chlorides also dissolve readily in dry chloroform to a clear colorless solution. If this solution is allowed to

there results finally a quantity of colorless needles similar in appearance to a much greater quantity of colorless oil. If care is taken to avoid shaking the mixture or elevating the temperature, these needles

soluble than the oily mother-liquor. If the

to rise even a few degrees, the needles are

at once redissolved. If the

from which the crystals have been removed

is redissolved in chloroform and allowed the solution

to evaporate under exactly the same

conditions as before no further crystallis-

ation is obtained – the final result being

in all cases a colorless oil.

The Benzenes. –

– The chlorides also dissolve in boiling

benzine (b.p. 80°) to a colorless solution, but

however, the oil is allowed to stand in con-

can also be separated mechanically and washed. No further crystallisation of the mother-liquor can be obtained.

IV Behavior of the Chloride towards Cold Water.

water. If however the insoluble oil is allowed to stand undisturbed under water for [illegible] of obtaining the crystals. A layer of the Chloride

[illegible] used, is covered with considerable cold water and set aside in a cool place until no further increase in the amount [illegible] are then rapidly poured off, care being taken to avoid raising the temperature the crystals which cling to the bottom

of the usual washing fluids with a few drops of water and freely with a small quantity of ether.

4 Behavior of the Dipetallic Chloride towards

ether, chloroform or benzine. They engage each again readily and completely. For the former two the benzene not

Kept

ch the and re-solidify

These crystals

sis gave the following results: -

I. .2015 gram of substance gave .2393 gram of Silver Chlo-
II. .2205 gram of substance gave .2621 gram of silver chlo-

	Calculated for $C_7H_{14}SO_3Cl_2$	Found. I	II
Cl	= 29.65 %	29.46 %	29.4 %

These facts are given in detail in order to show that the product of the action of phosphorus pentachloride upon salts of ortho-

chloric [illegible] is a single individual. The formulas can [illegible]

two compounds - one a solid, the other an oil capable of dissolving the solid. As this view is supported by the chemical behavior of the bromide the terms liquid and solid will be used to distinguish the two constituents of the mixture, while the term impure

the Turbine products.

Behavior of the [illegible]

very decided odor resembling that of benzoyl chloride was observed. When hot water was added to the dark colored liquid it solidified almost completely, the odor of benzoyl chloride [illegible] the same time. The mass was

I. When heated alone the chloride begins to decompose slowly at 150°. The decomposition increases in rapidity as the temperature is raised until the boiling point of chlorbenzoyl chloride is reached where it is complete in a very short time. The principal reaction is probably represented by the equation—

$$C_6H_4SO_3Cl_2 = C_6H_4ClCOCl + SO_2,$$

while a secondary reaction gives rise to

The decomposition is not affected by the presence of phosphorus oxychloride.

The reaction lowering the initial temperature of reactions material formed by secondary reactions. The reaction is probably represented by the equation

$$C_6H_4SO_3Cl_2 + PCl_5 = C_6H_4(COCl)_2 + Cl_2$$

11 That in the reaction between phosphorus pentachloride and salts of orthosulphobenzoic acid, a by-product free from any desulphonation products can be readily obtained by avoiding the excess of phosphorus pentachloride and temperatures above 100°.

recrystallized from boiling water until its melting-point showed it to be pure. This was then saponified with a dilute solution of caustic potash and the aniline liberated, redistilled. As the loss and so the aniline of the laboratory was found to give the same results. The latter was used in most of the experiments.

I. Action of Aniline on the Tissues of Water.—

—32 grams of aniline were added to 20 grams of [in an emulsion] ~~water~~. The mixture was shaken until no more aniline was [illegible]. The [illegible] the insoluble portion dried, powdered, and extracted with boiling ether. The ethereal solution on evapo-

was the insoluble anilide of orthosulphobenzoic acid in a tolerably pure condition. The filtrate from the portion insoluble in water was evaporated to a small volume and allowed to cool, a considerable quantity of pure white needles crystallised out. On further evaporation a crystalline substance crystallised out which it was impossible to purify, those evaporated to dryness, the residue powdered and extracted with boiling ether. The ethereal solution contained only unchanged orthosulphobenzoic acid. The residue insoluble in ether gave, on recrystallisation from water, a white substance which was the anilide of orthosulphanilidobenzoic acid. The proportion in which the different

0.1 grams of infusible anilide corresponding to 64.5% chloride,
0.1 grams infusible anilide corresponding to 22.9% chloride,
0.1 grams of K.Cl. salt corresponding to 9.9% chloride,
Not accounted for 4.5% chloride.

ii Action of urea upon the fatty anilides.—

— Urea was gradually added to 20 grams of chloride until a decided odor of ammonia remained after the mixture had been warmed on the water bath for some time. Water was then added to the mass. The excess of urea

insoluble in ether was extracted with a boiling mixture of alcohol and ether. The solution contained the infusible anilide.

which separated out almost completely, and
very small portion of the chloride which
remained in solution. The small portion of
substance insoluble in ether mixture gave
on recrystallization from water the anilide
salt of ortho-sulphamidobenzoic acid mentioned
above. The proportions of the substances formed
are as follows;

19.2 grams infusible anilide corresponding to 66.2% Chloride

III Action of Aniline upon the pure Salt in the Presence of Water. —

2 grams of the crystalline chloride were
powdered and suspended in water. A
was then added until it was no longer taken
up. The reaction was very slow. The product

was treated as in Exp. I. Only the fusible anilide was obtained. The yield was 7.5 of the theoretical. This experiment was frequently repeated but nothing but the fusible anilide

IV. Action of aniline upon the solid Chloride. —
— About 2 grams of the solid chloride were melted on the water-bath and aniline added until it was in slight excess. The [illegible] was treated as in Exp. II. Only the anilide aniline-hydrochlorate were obtained. This experiment was [illegible]

X Action of aniline upon [illegible] Chloride obtainable. —
— Portions of the chloride from which the solid constituent had been removed as completely as possible by means of chloroform [illegible]

but the relative quantities in which they

In the presence of water the amount of in-
fusible nitride formed corresponded to 85%
the chloride and in the experiment with
the dry substances it corresponded to 80.5%
like those obtained by a study of the be-
havior of the chloride towards different sol-
vents lead to the conclusion that it is
a mixture of two substances and that
the isomerism observed in the nitrides, what-
ever its nature, is to be referred to similar
relations between these two chlorides. The
experiments show conclusively that the solid
chloride gives no infusible nitride no-
matter under what conditions nitrides

is allowed to react with it, and that, on the other hand, the insoluble anilide is invariably formed when aniline reacts with a chloride which contains some of the difficult material, [illegible] removed from the mixture.

The Aniline Products.

1. The Anil.—

—As formed by [illegible] derivative of ortho-acid obtained by the action [illegible] chloride being the second product. It may be expressed by the equation:

$$C_6H_4 \begin{matrix} COCl \\ SO_2Cl \end{matrix} + 3C_6H_5NH_2 = C_6H_4 \begin{matrix} CO \\ SO_2 \end{matrix} > N.C_6H_5 + 2C_6H_5NH_3Cl$$

It has also been shown that it is formed in small quantities by the action of

dry aniline upon the mixed chlorides, and it will be shown later that it is also formed by the action of phosphorous [illegible] benzoic acid. Its properties have been adequately described by Coates. It is difficult to get it absolutely pure. When recrystallised from alcohol it invariably softens at 180°-185° and then melts finally at 190°. The best results were obtained by recrystallising it from a mixture of alcohol and ether. A specimen obtained in this way, gave, on analysis, the following [illegible]:

I .2103 gram substance gave .4633 gram CO_2 & .0760 gr. H_2O

II .2181 gram substance gave .4809 gram CO_2 & .0725 gr. H_2O

III .1085 gram substance gave .0988 gram $BaSO_4$.

IV .1562 gram substance gave .1403 gram $BaSO_4$.

Calculated for $C_6H_4 < \overset{O}{\underset{SO_2}{>}} N.C_2H_5$	Found					
	I	II	III	IV	V	VI
C = 60.22	60.08	60.13	—	—	—	—
H = 3.47	4.02	3.69	—	—	—	—
			—	12.41	12.51	

In its chemical properties it closely resembles the meta-substituted benzoic sulphimide. When boiled with dilute hydrochloric acid for several hours it undergoes decomposition. On evaporating the solution to a small volume long colorless needles are obtained which, as shown by analysis, consist of the acid amidic salt of ortho-sulphobenzoic acid; which was also obtained by Traub[1] by the action of one molecule of ammonia upon one molecule of ortho-sulpho-

[illegible]

[illegible]

[illegible]

Calculated for $C_6H_4 < \begin{matrix} COOH \\ SO_2NH_2 \end{matrix}$ C_6H_5.

S 10.52 10.6 10.65

Potassium salt of orthosulfobenzoic acid anhydride and the solution is boiled with dilute hydrochloric acid:- $C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH + 2H_2O = C_6H_4 < \begin{matrix} COOH \\ SO_2ONH_4 \end{matrix}$.

SO_2.

As stated by Traube, the acid is insoluble in dilute alkalies, but goes into solution on boiling. From this solution acids precipitate an acid which on heating passes back into the acid. This acid was also prepared by the

following reactions which show its structure and that of the acid obtained from it.

When orthotoluene sulphon chloride is treated with aniline, orthotoluene sulphonanilide is obtained according to the equation:

$$C_6H_4 < \begin{matrix} CH_3 \\ SO_2Cl \end{matrix} + 2C_6H_5NH_2 = C_6H_4 < \begin{matrix} CH_3 \\ SO_2NHC_6H_5 \end{matrix} + C_6H_5NH_2.HCl$$

In this compound the aniline residue

When orthotoluene sulphonanilide is oxidised it

according to the equation:-

$$C_6H_4 < \begin{matrix} CH_3 \\ SO_2NHC_6H_5 \end{matrix} + 3O = C_6H_4 < \begin{matrix} COOH \\ SO_2NHC_6H_5 \end{matrix} + H_2O$$

In this acid the aniline must also be in

combination with sulphur and it was

found identical with the acid obtained

from the anil by the action of alkalies.

to the equation: $C_6H_4 < \begin{matrix} COOH \\ SO_2NHC_6H_5 \end{matrix} + C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} > NC_6$

those by which benzoic sulphinide was first obtained by Remsen and Fahlberg:

1) $C_6H_4 < \begin{matrix} CH_3 \\ SO_2Cl \end{matrix} + 2NH_3 = C_6H_4 < \begin{matrix} CH_3 \\ SO_2NH_2 \end{matrix} + NH_4Cl$.

2) $C_6H_4 < \begin{matrix} CH_3 \\ SO_2NH_2 \end{matrix} + 3O = C_6H_4 < \begin{matrix} COOH \\ SO_2NH_2 \end{matrix} + H_2O$.

3) $C_6H_4 < \begin{matrix} COOH \\ SO_2NH_2 \end{matrix} = C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH + H_2O$.

The passage from the amido acid to the acid is, however, by no means so easy [illegible] to the sul-
imide transformation by boiling is not satisfactory, as at the high temp-
erature [illegible] some carbon dioxide is given off. With the aid of
[illegible] the change can be made readily and cleanly
at the ordinary temperature. For this pur-
pose [illegible] is treated with
chloroform and phosphorus pentachloride
added to the solution. The evolution of
hydrochloric acid begins at once and

the reaction is complete in a few minutes. By distilling off the chloroform and the chlorides of phosphorus as completely as possible under diminished pressure, and crystallizing the residue from a mixture of [illegible], the acid is obtained at once. It was impossible to obtain the intermediate chloroanilide. The reaction in all probability takes place

[illegible]

(2) $C_6H_4\langle^{COOC_2}_{SO_2NH.C_6H_5} = C_6H_4\langle^{CO}_{SO_2}\rangle N.C_6H_5 + HCl.$

These reactions leave no doubt that the substance is the symmetrical acid chloride of sulphobenzoic acid, and, as it is formed quantitatively from the solid chlorides, the mode of formation is such that the latter is the symmetrical dichloride of orthosulphobenzoic acid represented

by the formula $C_6H_4 < \overset{CO}{\underset{CO}{}} > NH$. It has been shown also that the fusible anilide is the only product upon this chloride in the presence of water. This ~~used~~ leads to the conclusion that the fusible anilide is the symmetrical diamilide of orthosulphobenzoic acid — a conclusion which, as will be shown later, is confirmed by the behavior of the anhydrides.

Action of Aniline upon Orthosulphobenzoic.

[illegible] all in a current of steam, and the oil is [illegible] maximum. If, however, it is boiled for a few hours, and the aniline then distilled off with steam, the residue, when [illegible] from alcohol, gives beautiful anilide the calculated quantity. This

experiment was repeated under modified conditions, as it was important to determine whether

formed by the direct addition of acidine to the asymmetrical acid. Nothing

fusible acidide could ever be obtained. The reaction is doubtless analogous to that between acidine and benzoic

$$C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH + C_6H_5 \cdot NH_2 = C_6H_4 < \begin{matrix} CO\ NH \cdot C_6H_5 \\ SO_2\ NH_2 \end{matrix}$$

$$C_6H_4 < \begin{matrix} CO \\ SO_2 \end{matrix} > NH + C_6H_5 \cdot NH_2 = C_6H_4 < \begin{matrix} CO\ NH \cdot C_6H_5 \\ SO_2\ NH_2 \end{matrix}$$

The fusible Acidide.

This acidide is formed quantitatively by

in the presence of water. It is also formed

of water and is obtained in small amounts by the direct addition of to the

anil. The general properties of the substance

.1347 gram substance gave .3200 gram CO_2 and .0559 gm. H_2O.

.1842 gram substance gave .4240 gram CO_2 and .0808 gram H_2O.

.2008 gram substance gave .1311 gram $BaSO_4$.

1417

Calculated for $C_{14}H_{13}CONHC_6H_4-$		Found.			
64.77	64.9				
4.67	4.95	—	—		
—	—	9.22	9.26		—
		—	—		

The chemical behavior of this substance is throughout that of an acid anilide. When boiled with dilute hydrochloric acid it readily goes into solution. From this solution there is obtained on concentration

[illegible] ...ther, a smaller quantity of the [illegible] ...from water, was obtained as [illegible] ...and, on [illegible] ...lysis and sublimation, gave [illegible] ...of the acid anilide salt of o-chlorobenzoic acid, which was also obtained by [illegible] ...of the acid.

A sulphur determination gave the following results:

I. 0.1470 gram substance gave 0.1270 gram $BaSO_4$

II. 0.1410 gram substance gave 0.1110 gram $BaSO_4$

Calculated for $C_6H_4 \begin{cases} SO_3NH_3C_6H_5 \\ COOH \end{cases}$	Found. I	II
S 10.76	10.8	10.86

The leaflets on recrystallization from water melted at 192°; gave [illegible] on addition of cold alkalis, and were undoubtedly ortho-sulphobenzoic acid, the decomposition

If the solution obtained by fusion is boiled for a short time and then acidified with mineral acid, sulphobenzoic acid precipitated by the action of alkalies upon ortho-toluene sulphonamide, is obtained. It is readily recognized by its crystalline form and melting-point. The decomposition generally goes further and a small quantity of acid

If a strongly alkaline solution is boiled for

30 hours (or, if necessary, the decomposition into the substances out of which benzoic acid is formed is complete, all the sulphur passing off

the fusible amides decomposes in two stages

$$C_6H_4 \begin{cases} CO\,NH\,C_6H_5 \\ SO_2\,NH\,C_6H_5 \end{cases} + KOH = C_6H_4 \begin{cases} CO\,OK \\ SO_2\,NH\,C_6H_5 \end{cases} + NH_2C_6H_5 .$$

$$C_6H_4 \begin{cases} CO\,NH\,C_6H_5 \\ SO_2\,NH\,C_6H_5 \end{cases} + KOH = C_6H_4 \begin{cases} CO\,OK \\ SO_2\,NK \end{cases} + NH_2C_6H_5 .$$

alkalies are known also of acid amides, while the fact that the decomposition with alkalies takes place in two stages is

with the two amidine residues bear a different relation to the molecule. This leads to the structure $C_6H_4 \begin{cases} CO\,NH\,C_6H_5 \\ SO_2\,NH\,C_6H_5 \end{cases}$ which represents one amidine residue united with carbon and the other with sulphur. As will be shown later, it is much more difficult to saponify a sulphonamide than the

N. g carbonic amide. N

be expected that a substance having this structure would, under proper conditions, lose

finish the amides residues combined with carbon, and eventually all the amidic. That this takes with the fusible amide is shown by the fact that the product with chemical condensa-
by loss of amide combined with sulph
Taking all these facts into consideration —
the formation from the chlorides which under
conditions gives only symmetrical anhydrosulphe
hoi and the conversion into the symmetrics"

from the symmetrical by retention of amidic
to that of one unit amide, and its decomposi
Into its two stages — there can be no reaso-
nable doubt that the fusible amide
benzoic acid, and that its structure is
by the formula. $C_6H_5 \cdot CO \cdot NH \cdot C_6H_5$,

The Preparation of Amides.—

amide is invariably the main product of the action of ammonia upon the ethereal chlorides. The best way to purify it is to recrystallise it from boiling water in which it is much more soluble than

ponded and from which it crystallises in beautiful colorless needles. prisms. An analysis of the substance prepared in this way gave the following results

.2802 gram substance gave .1867 gram $BaSO_4$.

.2051 gram substance gave .1376 gram $BaSO_4$.

.1231 gram substance gave .2798 gram CO_2 and .053 gram H_2O

ance gave .3097 gram CO_2 and .0573 gram H_2O

— — 64.9% 64.8 — —

In its chemical behaviour the infusible anilide is characterised by a remarkable resistance to the action of most reagents. [illegible] prolonged boiling with dilute sodium hydroxide solution does not appear to convert the fusible anilide and the acid into the sodium salt of orthosulphobenzoic acid, it also goes into solution but crystallises out unchanged on cooling. The result is the same no matter what the concentration of the acid or what the temperature used. Thus in a typical experiment it was heated in a sealed tube with concentrated hydrochloric acid and the tube allowed to [illegible] boiling point of mercury. After heating at this temperature for ten hours, it crystallised out unchanged on cooling. The infusible anilide can not be decomposed by hydro-

chloric acid.

The infusible acidide dissolves very slowly in dilute alkalies, but no matter how long the solution is boiled, or how concentrated ~~it~~ may be the alkali used, or whether a water or an alcoholic solution is used, acids invariably reprecipitate the unchanged acidide.

It dissolves readily in concentrated nitric acid and in fuming nitric acid but separates with a mixture of concentrated nitric and sulphuric acids. When boiled with fuming nitric acid, however, it is decomposed [illegible] be obtained from the solution.

The [illegible]

infusible anilide was boiled with benz-

distilled off as completely as possible under diminished pressure, and the residue boiled with water. The product difficultly soluble in water was found to be benz-anilide. Its identity was established by with benzanilide prepared from benzoyl chloride and aniline. It was

olate the other products of the reaction. It was, however, found that when aniline is added to this product the infusible anilide is formed, indicating that the action

of benzanilide shows that the infusible

acetide contains acetic residues as weak and in its formation as might be judged to have taken place from its indifference towards most reagents. This same result is reached by the formation in a chloroform solution and the following way. The products of the reaction are now under investigation. It can, however, be said with certainty that one of the products of the action is the pyruvic acid.

The experimental evidence thus far obtained with reference to the structure of the insoluble acetide is also too small to justify any conclusion in regard

sulphobenzoic acid formed by the action of aniline upon the mixed chlorides. It is formed due to a secondary reaction. It crystallizes moist, rapidly becomes colored in the air. It is readily soluble in water and alcohol, gave the following results:-

.1850 gram substance gave .1178 gram $BaSO_4$.

.1624 gram substance gave .1045 gram $BaSO_4$.

Calculated for

$C_6H_4 < \begin{matrix} CO.OH_2C_6H_5 \\ SO_2NHC_6H_5 \end{matrix}$

Found

I II

It was first prepared by adding a calculated quantity of aniline to meta-

of preparation shows that its structure.

$$C_6H_4\begin{cases}CO\\CO\end{cases}NH + 2C_2H_5ONa + H_2O = C_6H_4\begin{cases}CO.ONa\\CO.NH.C_2H_5\end{cases} + C_2H_5NH_2.$$

no effect upon the sulphonamides. 5 grams

other is due to the fact that the former is connected with carbon and the latter with [illegible]

[illegible]

This reduction was effected by combining [illegible] with [illegible] which [illegible] [illegible] [illegible]

the acetate in a solution of caustic potash
5 grains of orthotoluenesulphonamide were dis-
grains of caustic potash, and the solution heat-
the color of the ferrocyanide had en-

because the amides would be partially decomposed by concentrating the alkaline solution. The

and acidified with concentrated hydrochloric acid. This precipitated both the remainder of the unused amides and the amidic acid formed.

use by means of absolute alcohol. The solution containing the barium salt was

water and the free acid separated by acidifying with hydrochloric acid. One recrystallisation of the acid prepared in this way gave a perfectly pure substance which melted sharply in hot water and very difficultly soluble in

its composition is $C_{13}H_{11}O_4N_3$, and the reaction is represented by the formula $C_6H_4<^{CO_2H}_{CO_2NHC_6H_5} - H_2O = C_6H_4<^{CO}_{CO_2NHC_6H_5}$.

Salts of Orthosulphamidobenzoic Acid.

Salts prepared as mentioned

above crystallizes in small colorless needles which show no tabular forms. The analysis gave the following results:

.2001 gram substance gave .0674 gram $BaSO_4$.

.2255 gram substance gave .1763 gram $BaSO_4$.

Calculated for	Found	
$\left(C_6H_4 < \begin{matrix} CO.O \\ SO_2 \end{matrix} NHC_6H_5\right)_2 Ba$	I	II
Ba. 19.88	19.8	19.91

Conclusion.

Briefly stated, the results obtained by this investigation are as follows:—

I The product of the action of phosphorus pentachloride upon salts of ortho-sulphobenzoic acid is a mixture of two chlorides, one of which is a solid, the other a liquid.

Biographical Sketch.

The writer was born at Egypt Pa. on Nov. 6 [illegible]

November 1881 and Muhlenberg College in October 1882. After taking the regular graduate course he received the degree of Bachelor of Arts in 1886 and that of Master of Arts in 1889. In October 1889 he entered the Johns Hopkins University where he has [illegible]